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Determination of the effective magnetic anisotropy constant of ferrite nanoparticles dispersed in organic matrix

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Abstract : With increasing interest in realising new magnetic materials, the magnetic behaviour of the nanoparticle disperse systems became an important problem both from the experimental point of view and from the theoretical one The researches performed in the last period show that, by controlling the size distribution, the effective anisotropy constant and the nanoparticle concentration, the nanoparticle disperse systems can be used for realising magnetic materials with special properties This paper presents a modality to determine the effective anisotropy constant of the mixed ferrite nanoparticle of NiZn, dispersed in the solid organic dielectric matrix – Nestrapol 450 In this respect, there are realised samples with low nanoparticle concentration, which are studied in dynamic magnetic fields through the *Q*-metric method, using a coaxial transmission line in short-circuit So, it can determine the dependence of the complex magnetic permeability components, the tangent of the magnetic loss angles and material quality factor, on the frequency, and then we can calculate the medium Néel relaxation time and the effective anisotropy constant of the nanoparticles

Keywords : Fine-particle systems, magnetic properties, nanoparticles, composite materials

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1. Introduction

For a given substance, the effective magnetic anisotropy constant depends on the method of nanoparticle generation. So, for the magnetite nanoparticles, Raiker and Shliomis [1] indicate values of this constant in the range 10^3–10^4 J/m^3. In the same time, Kneller presents [2] values determined by many authors, refer to the effective magnetic anisotropy constant of massive samples, at room temperature. They set in the range $(7.3–14)\cdot10^3$ J/m^3. For the mixed ferrite nanoparticles of ferro-fluids types $Mn_{0.4}Zn_{0.6}Fe_2O_4$ and $Mn_{0.4}Zn_{0.6}Fe_2O_4$, the effective magnetic anisotropy constants have been determined [3] (values found : $1.9\cdot10^3$ J/m^3 and $1.3\ 10^3$ J/m^3). In case of mixed

ferrites, Dillon [4] indicates the value $7.2 \cdot 10^3$ J/m^3 for the anisotropy constant of a sintered ferrite sample of NiZn.

In the magnetisation process of a nanoparticle system dispersed into a solid matrix, the magnetic moment rotation dependents on the nanoparticle, this one remaining fixed. Owing to this mechanism, there appears a Néel relaxation moment [5] associated with the magnetic moment rotation, inside the nanoparticle, the corresponding relaxation time being correlated with the material properties of the particles. In case of a low nanoparticle concentration, so that we can neglect the dipole magnetic interactions among the nanoparticles, the expression of the Néel relaxation time has been established by Brown, in the form [5] :

$$\tau_N = \tau_{0N} \exp\left(\frac{KV}{k_B T}\right), \tag{1}$$

where V is the volume of the particle magnetic core. In the relation (1), based on the study presented in the paper [2] :

$$\tau_{0N} = \sqrt{\frac{\pi}{4\sigma^3}} \cdot \tau_{Bi}, \tag{2}$$

where $\sigma = \frac{KV}{k_B T}$, K = effective magnetic anisotropy constant of the nanoparticles, V = average volume of the nanoparticle, k_B = Boltzmann constant, T = absolute temperature, and τ_{Bi} = relaxation time "inherent Brown", introduced due to the analogy between the rotation motion of the magnetic moments, inside the particle, and the Brown rotation of the particle :

$$\tau_{Bi} = \frac{3\eta_m V}{k_B T}, \tag{3}$$

where η_m is "the internal magnetic viscosity" which depends on the nature of the material. Replacing (3) in (2) and taking into account the expression of the non-dimensional ratio σ, it results :

$$\tau_{0N} = \frac{3\eta_m}{2K}\sqrt{\frac{\pi k_B T}{KV}}. \tag{4}$$

The motion of the magnetic moments in the magnetic field $\boldsymbol{H}$, *versus* the crystal axes of the particles, is described by the equation Landau-Lifschitz [1] :

$$\frac{d\boldsymbol{m}}{dt} = -\gamma(\boldsymbol{m} \times \mu_0 \boldsymbol{H}) - \frac{\alpha\gamma}{m}\left[\boldsymbol{m} \times (\boldsymbol{m} \times \mu_0 \boldsymbol{H})\right], \tag{5}$$

where α is a non-dimensional damping constant and γ is a gyromagnetic factor. In a constant field, the first term (from right) of the relation (5) represents the free

precessional motion of the magnetic moments around the ***H*** direction with Larmor frequency $\omega_L = \gamma\mu_0 H$ The second term, which represents a vector directed from the magnetic moment direction to the applied field direction, determines the reduction of the precession angle The time when the magnetic moments direction overlaps the field direction is exactly the Neel relaxation time τ_N The factor $b_r = \frac{\alpha\gamma}{\mu_0 m}$ in the relation (5) represents the rotational mobility of the magnetic moments Therefore, for the rotational diffusion coefficient of the vector ***m***, according to Einstein's formula [2], we have $D_r = b_r k_B T = \frac{\alpha\gamma k_B T}{\mu_0 m}$ Taking into account the definition of the diffusion time $\tau_{Br} = (2D_r)^{-1}$ and the relation for the magnetic field of the monodomain particle ($m = VM_s$, where M_s is the saturation magnetisation of the solid material which the particle comes from), we obtain .

$$\tau_{Br} = \frac{\mu_0 M_s V}{2\alpha\gamma k_B T}. \tag{6}$$

From (3) and (6), we get the explicit expression for the magnetic viscosity

$$\eta_m = \frac{\mu_0 M_s}{6\alpha\gamma} \tag{7}$$

By introducing (7) in (4), for τ_{0N} we obtain the expression

$$\tau_{0N} = \frac{\sqrt{\pi}}{2}\ \tau_0 \sigma^{1/2} \tag{8}$$

with

$$\tau_0 = \frac{\mu_0 M_s}{2\alpha\gamma K} = (\alpha\omega_L)^{-1} \tag{9}$$

which represents the relaxation time of the precessional motion in the anisotropy field H_a. If, at the moment $t = 0$, the vector ***m*** deviates from the low magnetisation direction with an angle θ_0, then, under the action of the anisotropy field, the angle between ***m*** and $\boldsymbol{H_a}$ varies in time, according to the relation .

$$\theta(t) = \theta_0 \exp \tag{10}$$

If we introduce (8) in (1), we obtain the Néel relaxation time [5]

$$\tau_N = \tau_{0N}\ \exp\sigma = \frac{\sqrt{\pi}}{2}\ \tau_0\ \sigma^{-\frac{1}{2}} \exp\sigma\,, \tag{11}$$

where τ_0 is given by the relation (9) and $\sigma = \frac{KV}{k_B T}$.

The relaxation processes involve dissipative processes that are described by the dependence of the imaginary component χ'' of the complex magnetic susceptibility on the field frequency. According to Debye [6], the Néel relaxation time is correlated with the angle frequency ω_{max}, where χ'' is maximum according to the relation :

$$\omega_{max}\tau_N = 1. \quad (12)$$

As example, we will realise a sample with low concentration of mix ferrite NiZn. Through a *Q*-metric method, using a line with short-circuit transmission as sample, we will determine the dependence of the imaginary component χ'', complex magnetic susceptibility or the imaginary component of the complex magnetic permeability μ'' on the applied field frequency. From the dependence graph $\mu'' = f(f)$, we will determine the frequency that corresponds to the peak of the curve. We will introduce the value of this frequency in the Debye relation (12) to determine the average Néel time for the magnetic relaxation and then, from the relation (11), through graphical plotting, we will determine the effective average magnetic anisotropy constant of the nanoparticles.

2. Sample preparation

The sample is made of nanometric dielectric ferrite powders, having organic nature. The nanometric powder is mix ferrite NiZn, $Ni_{0,2}Zn_{0,8}Fe_2O_4$, obtained through atomisation, with the average magnetic diameter of 13 nm, having spontaneous magnetisation M_s = $2.85 \cdot 10^5$ A/m. The used organic matrix is Nestrapol 450, an unsaturated polyester resin in liquid state. During mixing and homogenising the powder-Nestrapol mixture, we added a plasticiser – cobalt naphthenate and a hardener – butanox (peroxide of methyl-ketone), and then the mixture was poured in moulds. The mixture solidified in the moulds in few hours, at the room temperature, depending on hardener quantity. We obtained a toroid sample, with the length smaller than the length of the coaxial transmission line used in the measuring installation. The apparent volumetric fraction (the volume occupied by the unpressed powder spread in the sample volume) is 0.7335 and the real one is 0.3836.

3. Method for measuring the complex magnetic permeability in a radiofrequency field

Experimental results

To determinate the components of the complex magnetic permeability, we used a *Q*-metric method [7] based on the determination of the complex impedance of the sample, $z_s = R_s + jX_s$ with the help of the short-circuit transmission coaxial line technique. In case the transmission line is not full of material, the method presented

in [3] and [8] may be used, applied for fluids. The equivalent circuit of the short-circuit transmission coaxial line, discharged on the charge impedance z_s is presented in Figure 1, and the line model is presented in Figure 2.

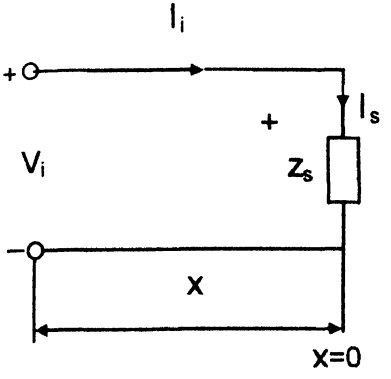

Figure 1. The equivalent circuit of the transmission line discharged on the charge impedance z_S.

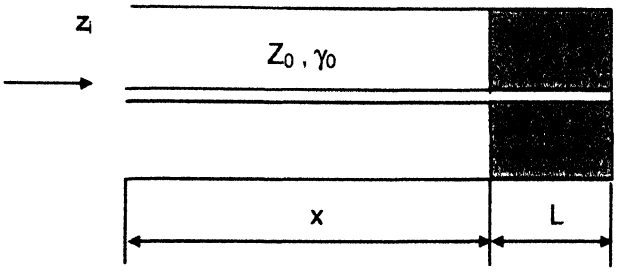

Figure 2. The model of the transmission coaxial line in short-circuit, discharged on a toroid sample.

The feed impedance of the transmission line at the distance x from the charge (Figure 1) is given by :

$$z_i = \frac{V_i}{I_i} = \frac{V_s \cosh(\gamma_0 x) + z_0 I_s \sinh(\gamma_0 x)}{I_s \cosh(\gamma_0 x) + \frac{V_s}{z_0} \sinh(\gamma_0 x)} . \tag{13}$$

That can be written as :

$$z_i = z_0 \frac{z_s + z_0 th(\gamma_0 x)}{z_0 + z_s th(\gamma_0 x)} , \tag{14}$$

where z_0 is the characteristic impedance of the empty line (with air) with

$$z_0 = \frac{z_{m0}}{2\pi} \ln \frac{D}{d} = \sqrt{\frac{\mu_0}{\varepsilon_0}} \cdot \frac{1}{2\pi} \ln \frac{D}{d} , \tag{15}$$

where D and d are the outer and, the respective, inner diameter of the transmission line, and γ_0 is the propagation constant that can be written :

$$\gamma_0 = \alpha + j\beta \tag{16}$$

with $\alpha \rightarrow$ the attenuation coefficient, $\beta = 2\pi/\lambda \rightarrow$ phase factor and $\lambda \rightarrow$ wavelength in line. In case the losses in line are very low $\alpha \cong 0$ and $\gamma_0 = j\beta$, the eq. (14) becomes :

$$z_i = z_0 \frac{z_s + j z_0 tg(\beta x)}{z_0 + j z_R tg(\beta x)} . \tag{17}$$

In the methods presented in the papers [3] and [8], the relation used is type (17). Thenceforth, we will take into account also the attenuation coefficient from the propagation constant. In case of coaxial air line in short-circuit, with the length l, $z_s = 0$ and $V_s = 0$. And, from the relation (14), the feed impedance becomes :

$$z_{l0} = z_0 th(\gamma_0 l). \tag{18}$$

From the relation (18), using the expression of the hyperbolic tangent,

$$th(\gamma_0 l) = \frac{e^{\gamma_0 l} - e^{-\gamma_0 l}}{e^{\gamma_0 l} + e^{-\gamma_0 l}}, \tag{19}$$

we obtain the propagation constant for the air line :

$$\gamma_0 = \frac{1}{2l} \ln \frac{z_{l0} + z_0}{z_0 - z_{l0}}. \tag{20}$$

Let's consider the case of a discharge coaxial transmission line, on a sample with the length L (Figure 2), where z_0 and γ_0 represent the characteristic impedance and the propagation constant for the air line. From the relation (14) we obtain :

$$z_s = z_0 \frac{z_l - z_0 th(\gamma_0 x)}{z_0 - z_l th(\gamma_0 x)}, \tag{21}$$

$$z_l = R_l + jX_l. \tag{22}$$

The values measured through the Q-metric method, Q_1, C_1, Q_2, C_2, for the coaxial line partially filled with magnetic material (Figure 2), are used in the relations [3], [8] :

$$R_l = \frac{1}{2\pi f}\left(\frac{1}{C_l Q_l} - \frac{1}{C_0 Q_0}\right), \tag{23}$$

$$X_l = \frac{1}{2\pi f}\left(\frac{C_0 - C_l}{C_0 C_l}\right). \tag{24}$$

For $i = 1$, without the sample, we obtain Ri_0 and Xi_0, and for $i = 2$, with the sample presence, we obtain the components R_{ip} and X_{ip} of the charge seen through the line with the length l. By gradually introducing the value pairs (R_{ip}, X_{ip}) and (R_{i0}, X_{i0}) in the relation (9) that takes into account the losses, inspite of the ideal relation (17), we obtain the impedance components of the line segment (with magnetic material),

$$z_{x_p} = R_{x_p} + jX_{x_p}, \text{ şi } z_{x_0} = R_{x_0} + jX_{x_0}, \tag{25}$$

Then, the real component of the magnetic permeability is $\mu' = \frac{X_{x_p}}{X_{x_0}}$, the tangent of the magnetic losses angle is $tg\delta_m = \frac{R_{x_p} - R_{x_0}}{X_{x_p}}$, the imaginary component of the magnetic

permeability is : $\mu'' = (\mu' + 1)tg\delta_m$ and the factor of material quality is $Q = \frac{1}{tg\delta_m}$. Experimental results for our sample are presented in Figure 3.

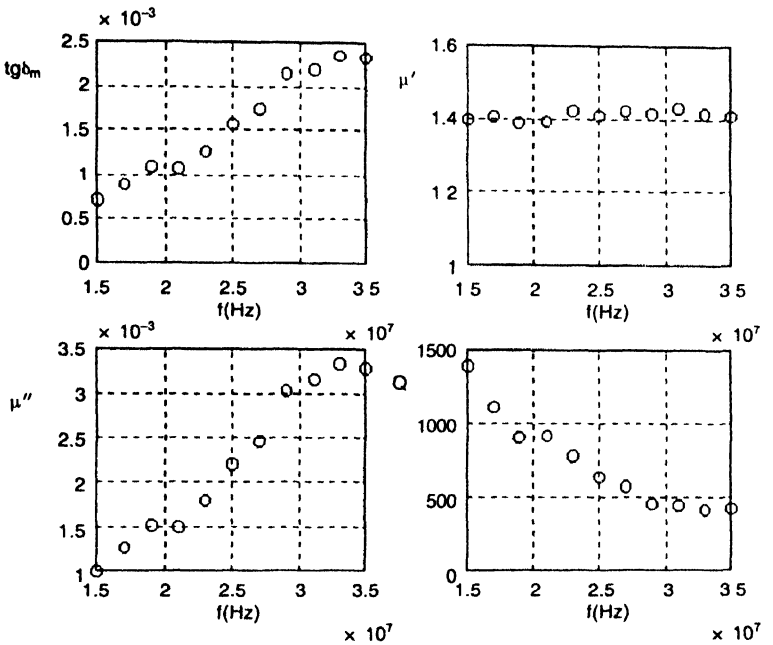

Figure 3. The tangent of the losses angle, the complex relative components of the magnetic permeability and the quality factor of the material are plotted against the frequency – for our sample.

Theoretically (Debye theory), it was shown that at the frequency when χ'' is maximum, the condition : $\chi_m'' = \chi_m'$ is effective, where χ_m' represents the value of χ' at the same frequency. But, after measurements, it was seen that $\mu_m'' < \mu_m'$, *i.e.* $\chi_m'' < \chi_m'$. This kind of deviation can be explained by the fact that only some particles of the magneto-dielectric material have a super paramagnetic behaviour. In Figure 3, it can be seen that the maximum imaginary component of the complex magnetic permeability is obtained at an average frequency of 34 MHz that corresponds, according to Debye relation, at the Néel relaxation time τ_N = 4.68 ns.

In order to determine the anisotropy effective constant of the sample nanoparticle, the Néel relaxation time (11) should be written [having in view also the relation (9)], as follows :

$$\frac{a \cdot \exp(b \cdot K)}{\tau_N \cdot K \cdot \sqrt{K}} = 1, \tag{26}$$

where $a = \frac{\mu_0 M_s \sqrt{\pi k_B T}}{4\alpha\gamma\sqrt{V}}$ and $b = \frac{V}{k_B T}$ are constants that can be calculated taking into

account the value of the giromagnetic factor $\gamma = 2.41 \cdot 10^5 s^{-1} A^{-1} m$ and the damping constant $\alpha = 0.02$ (for most ferromagnetic materials, α is around 10^{-2}). The relation (26) is a transcendental equation in the unknown K, whose solution can be graphically determined. Let f_1 be the numerator of the relation (26) and f_2 the denominator of the relation (26). At the room temperature, the graphical representation of the functions f_1 and f_2 is presented in Figure 4. The solution (the value of K) is the value where the two curves intercross (*i.e.* K = 6300 J/m^3).

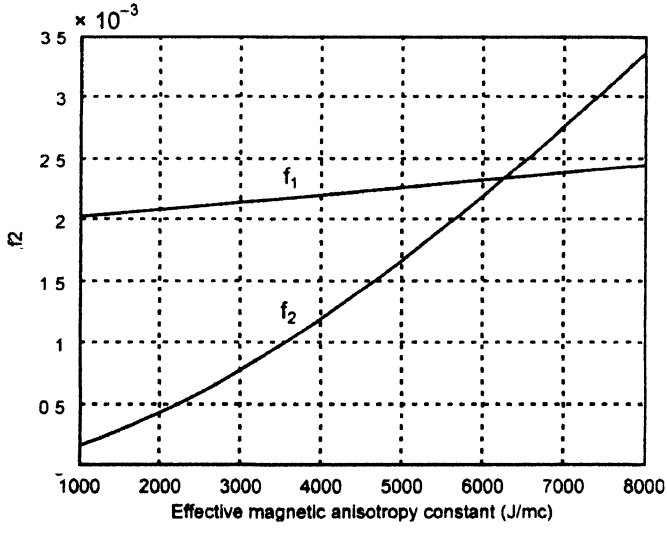

Figure 4. The graphical determination of the effective magnetic anisotropy constant of the mixed NiZn ferrite nanoparticles dispersed in solid organic dielectric matrix.

If we consider the particles to be spherical, identical and arranged into a cube tangent to nanoparticles, the maximum volumetric real fraction of nanoparticles, in case the powder is not pressed, is f_{max} = 0.523. According to Garcia relation [9], the maximum volumetric real fraction of nanoparticles, in case the powder is not pressed, is $f_m \quad 0.32 \cdot \frac{8K\pi}{\mu_0 M_s^2} = 0.523$, where μ_0 is the vacuum magnetic permeability. From this relation, we obtain a limit for K = 6637 J/m^3. It can be seen that there is a good correspondence with the value determined through the graphical method. The difference, between this value and the graphically obtained value, can be explained by the fact that the dispersed nanoparticles in Nestrapol 450 are not perfectly spherical.

4. Conclusions

The paper presents an experimental study of a composite material, in dynamic radiofrequency field, based on mixed NiZn ferrite nanoparticles and, in the same time, a method to determine the effective magnetic anisotropy constant of the nanoparticles dispersed in an organic dielectric solid matrix. The method takes into account the fact

that τ_{0N} (from the Néel relaxation time relation) depends on K [relation (9)] and it is not considered a constant with the value of 10^{-9} seconds, inspite of the claims in literature.

The scientific and technological importance of the dispersed magnetic systems of nanometric particles is justified by the possibility of realising advanced magnetic materials [10–16], from natural nanostructures to artificial nanostructures : ferro-fluids, medium of high density magnetic recording, magnetic sensors, hard and soft magneto-dielectric electro-technical materials, at usual and high frequencies ..

In all these cases, the special magnetic properties of the materials can be obtained through an adequate check of the effective magnetic anisotropy constant and the distribution of nanoparticle dimensions and concentration [17]

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